Chapter 5

Stable Isotopic Composition of Chlorine and Oxygen in Synthetic and Natural Perchlorate

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INTRODUCTION

Ammonium perchlorate has been used since the 1940s in the United States as a component of the solid propellant fuel for rockets and missiles. Perchlorate salts, which are strong oxidants, also are used in fireworks, munitions, air-bag inflation systems, highway flares, and matches. Past activities of the military and aerospace industries have led to widespread perchlorate contamination of groundwater.[1] Improvement of routine analytical methods used for the measurement of perchlorate in groundwater since 1997 have resulted in widespread detection of perchlorate throughout the United States in areas where perchlorate salts have been manufactured, stored, or used.[2-4] Lake Mead and the downstream Colorado River contain measurable levels of perchlorate[1]. Perchlorate has been detected in commercial food products, including vegetables and milk.[5,6] Although the total scope of perchlorate contamination in the United States remains unclear, recent estimates indicate that the drinking water supplies of 15 million people are affected by the contamination of the Colorado River alone.[7]

The potentially adverse human health effect of perchlorate ingestion makes it a major public health concern. Perchlorate inhibits iodide uptake by the thyroid causing disruption of normal thyroid function, which can lead to a number of serious health problems, especially pertaining to early neurological development.[8,9] In March 2004, California established a Public Health Goal of 6 µg/L for perchlorate concentration in drinking water, and other states have independently adopted advisory levels ranging from 1 to 18

μg/L. A special committee of the National Academies of Science (NAS) recently reviewed the toxicological data concerning perchlorate, and released a controversial report[10] that recommended a safe daily perchlorate dose more than 20 times higher than that endorsed earlier by the U.S. Environmental Protection Agency (USEPA).[11] The USEPA subsequently accepted the NAS recommendation and raised their reference dose from 0.03 to 0.7 μg perchlorate/kg body wt/day.

The perchlorate anion (ClO_4^-) consists of a central chlorine atom in tetrahedral coordination with four oxygen atoms. Perchlorate salts are soluble in water and some organic solvents. When dissolved in water, perchlorate is nonvolatile, stable and kinetically inert with respect to abiotic reduction and oxygen exchange. For example, the exchange of ^{18}O-labeled water with $HClO_4$ at a concentration of 9 mol/L was insignificant after 63 days at 100 °C, and the half-life for exchange at room temperature is estimated at greater than 100 years.[12] Perchlorate does not adsorb strongly to activated carbon and most mineral surfaces, and it is sufficiently unreactive that it cannot be effectively removed from water by conventional water treatment methods.[13] Perchlorate can be reduced in aqueous solution by some transition metal ions, such as Ti(III), Re(V), V(III), V(II), Mo(III), and Ru(II).[13]

A variety of different microorganisms have been isolated that can reduce perchlorate under anoxic conditions.[14] These organisms are currently being utilized in several full-scale bioreactor systems to remove perchlorate from groundwater at flow rates as high as 5,000 gallons per minute.[15,16] The presence of persistent plumes of perchlorate in groundwater aquifers indicates that biotic and abiotic reduction of perchlorate under typical oxic groundwater conditions does not lead to significant attenuation. However, the addition of a variety of different substrates is being used to stimulate perchlorate biodegradation in subsurface environments where the anion is otherwise long-lived.[16]

The perchlorate used for military and aerospace applications is synthesized by electrolytic oxidation of aqueous chloride brine. Although much of the known perchlorate contamination in the U.S. can be related to such industrial sources, there are some natural sources of perchlorate as well. The origin and abundance of perchlorate from natural sources is poorly known. The best known natural source of perchlorate is within the nitrate-bearing salt deposits of the Atacama Desert (Chile) that have been mined extensively for use as a nitrate source in agricultural fertilizers.[17] Perchlorate of apparent natural origin also has been detected in a number of ancient evaporite salt deposits,[18] and in modern rain and snow samples.[19] At several locations,

such as in the West Texas panhandle area, perchlorate of possible natural origin has been detected in ground water.[20]

The presence of natural sources of perchlorate in groundwater, whether through application of imported perchlorate-bearing fertilizers or from other more local but undefined sources, complicates the issue of liability for groundwater remediation near industrial sources of perchlorate. A practical forensic tool is thus needed that would enable the identification of the source(s) of perchlorate in contaminated aquifers and waterways. Successful applications of stable isotope ratio measurements of N and O in studies of nitrate, and C and Cl isotope ratios in studies of chlorinated solvents, have encouraged us to pursue the development of Cl and O isotopic analyses for tracing the sources and understanding the behavior of perchlorate in the environment. In this chapter, we review earlier isotopic studies of perchlorate and present new data to show that synthetic and natural perchlorates have distinct chlorine and oxygen isotopic compositions. We also present data for perchlorate extracted from groundwater samples that demonstrate the potential application of stable isotope ratio measurements for environmental forensics.

PREVIOUS ISOTOPIC STUDIES OF PERCHLORATE

The use of stable isotope ratio measurements for understanding the geochemical behavior of natural and anthropogenic compounds in the environment is a major field of research within the earth, atmospheric, oceanic, and environmental sciences. Recent developments in the measurement and application of the stable isotope ratios of carbon and chlorine in chlorinated aliphatic hydrocarbons led to important advances in characterizing the sources and behavior of these compounds in contaminated groundwater aquifers. Particularly important is the discovery that microbial degradation of chlorinated aliphatic hydrocarbons under aerobic and anaerobic conditions is accompanied by substantial kinetic isotope effects for both carbon and chlorine, allowing evaluation of the extent of biodegradation through measurement of isotope ratios. To date, however, few analogous isotopic studies of perchlorate have been published. The main reason for the paucity of published perchlorate isotopic data is that methods for precise isotope ratio measurements of chlorine and oxygen in perchlorate were not developed until about the past five years.[21-24]

Measurements of the kinetic isotope effect of microbial reduction of perchlorate in laboratory microcosms have been made for chlorine[22,25] and oxygen.[26] Data for the chlorine kinetic isotope effect observed in two microcosms of *Dechlorosoma suillum* JPLRND, which was initially isolated

from a groundwater sample collected in southern California, are shown in Fig. 1. The kinetic isotope effect measured for Cl is about 15‰. The preliminary value reported for the oxygen kinetic isotope effect[26] (~30 ‰) is about twice as large as that for chlorine. Similar measurements have not yet been made for abiotic reduction reactions. Such values may prove useful to determine if abiotic perchlorate reduction is a mechanism of loss in some groundwater environments.
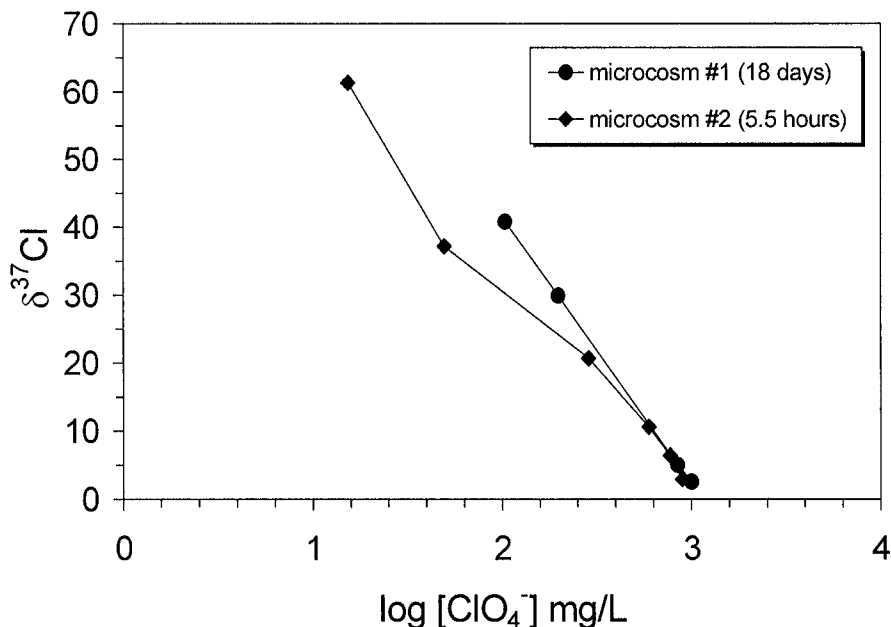

Figure 1. Isotopic composition of residual perchlorate ($\delta 37Cl$) as a function of the perchlorate concentration (mg/L) in two microcosm experiments using liquid cultures of *Dechlorosomas Suillum* JPLNRD[22]. Slopes of lines indicate a chlorine kinetic isotope effect of about 15‰. Analytical errors in $\delta^{37}Cl$ (±0.3 per mil) are smaller than symbols used for data points.

Evidence indicating that synthetic and natural perchlorates have distinct chlorine and oxygen isotopic compositions has been presented recently.[23,24] Oxygen isotopic evidence, especially the presence of ^{17}O in excess of that expected from mass-dependent isotopic fractionation, indicates that both nitrate and perchlorate in the natural Chilean nitrate-bearing salts are dominantly of atmospheric origin.[23,24,27,28] Their anomalous ^{17}O abundances may be attributed to oxidation reactions involving atmospheric ozone.

MATERIALS AND METHODS

Samples

Four types of perchlorate-containing materials were analyzed (Table 1):

(1) *laboratory reagents* from a number of suppliers;

(2) *commercial perchlorate salts and precursor materials,* including samples of NH_4ClO_4, $KClO_4$, and $NaClO_4$ were obtained from the American Pacific Corporation (AMPAC). In addition, AMPAC's perchlorate production facility (the Western Electrochemical Company in Cedar City, UT) supplied water, NaCl feedstock, and $NaClO_3$ and $NaClO_4$ electrochemical synthesis products from a single batch produced during June 2004;

(3) *natural perchlorate* extracted from samples of nitrate-bearing salt deposits from the Atacama Desert (Chile), and from commercial fertilizers derived from this material; and

(4) *groundwater and surface water* from sites in which significant concentrations of perchlorate were detected.

All laboratory reagents and production materials were analyzed as received. Perchlorate from groundwaters and from Chilean nitrate-bearing salts and fertilizers was extracted at Oak Ridge National Laboratory using a highly selective bifunctional anion exchange resin. The perchlorate was eluted in a solution of $FeCl_3$ and HCl, then precipitated by addition of CsCl or KCl to form $CsClO_4$ or $KClO_4$.[23,29] The purities of the purified perchlorate salts were verified by micro-Raman spectroscopy.

Several tests were made to ensure that the extraction procedures did not fractionate the isotopic compositions of Cl and O in perchlorate. First, a laboratory reagent of known isotopic composition (ORNL-6, hydrous Na-perchlorate) was added to a perchlorate-free, nitrate- and chloride-rich salt solution (the residue from extraction of perchlorate from an aqueous solution of a Chilean salt sample), and then the added perchlorate was extracted from this solution. The data for perchlorate recovered from this test (ORNL-15) had $\delta^{37}Cl$ and $\delta^{18}O$ values indistinguishable from those of ORNL-6 (Table 2). In another test, a sample of anhydrous Na-perchlorate reagent (UIC-1) was dissolved; the resulting solution (UIC-4) was later evaporated to dryness at 130°C. The $\delta^{18}O$ and $\Delta^{17}O$ values of this dehydrated perchlorate were indistinguishable from those of UIC-1. In a third test, an aliquot of 60 % perchloric acid (RSIL-2) was mixed with an equal volume of ^{18}O-enriched water ($\delta^{18}O$ = +254 ‰), and perchlorate from this solution was recovered after 38 days as Na-perchlorate salt (RSIL-3) following quick neutralization

Table 1.   Identification of perchlorate samples

Sample Identification	Compound	Description
Laboratory Reagents		
UIC-1	$NaClO_4$	Mallinckrodt lot # 1190KHJJ
UIC-2	$KClO_4$	Baker Analyzed lot # 45155
UIC-3	$NaClO_4 \cdot H_2O$	Aldrich lot # 00722CG
UIC-8	$KClO_4$	Sigma lot # 60K3451
UIC-9	$NaClO_4$	Sigma lot # 111K1334
UIC-10	$KClO_4$	Hummel-Croton
ORNL-6	$NaClO_4 \cdot H_2O$	EM lot # SX0693-2
ORNL-8	$KClO_4$	General Chem. Co. lot # 13
ORNL-9	$RbClO_4$	Aldrich lot # AN00625LZ
ORNL-10	$CsClO_4$	Aldrich lot # LI09119JI
ORNL-11	$CsClO_4$	Aldrich lot # 02407AS
RSIL-2	$HClO_4$	Baker 9656-1, lot # 146358
RSIL-4	$KClO_4$	Aldrich, lot # 11921HO
Production Materials		
UIC-5	$NaClO_4$	American Pacific Co. (N3300401)
UIC-6	$KClO_4$	American Pacific Co. (P0900402)
UIC-7	NH_4ClO_4	American Pacific Co. (A2000433)
ORNL-18	$NaClO_3$	Western Electrochemical Co. (TO403E)
ORNL-19	$NaClO_4$	Western Electrochemical Co. (TO403B)
ORNL-20	H_2O	Water used by WE (6/23/04)
NaCl (TO415D)	$NaCl$	NaCl feedstock used by WE
Natural Perchlorate		
ORNL-2	$KClO_4$	Commercial Hoffman fertilizer
ORNL-4	$CsClO_4$	Commercial Hoffman fertilizer
ORNL-5	$CsClO_4$	Atacama, Chile nitrate salt (AT-74-1)
ORNL-12	$CsClO_4$	SQM fertilizer (RSIL N7791)
Groundwater and Surface Water		
ORNL-14	$CsClO_4$	Groundwater at Edwards AFB, CA
ORNL-16	$CsClO_4$	Surface water, Las Vegas Wash
ORNL-17	$CsClO_4$	Groundwater, Henderson NV
ORNL-21	$CsClO_4$	West Texas groundwater (TTU-G1S)
ORNL-22	$CsClO_4$	West Texas groundwater (TTU-M3L)
CPMW-5*	$NaClO_4$	Indian Head, MD groundwater (2002)
TPMW-5*	$NaClO_4$	Indian Head, MD groundwater (2002)
Method Tests		
ORNL-15	$CsClO_4$	Prepared from ORNL-6
UIC-4	$NaClO_4$	Prepared from UIC-1
RSIL-3	$HClO_4$	Prepared from RSIL-2

* perchlorate extracted from Indian Head samples by method of Ref. 22

of the acid with concentrated NaOH. The $\delta^{18}O$ value of RSIL-3 perchlorate was indistinguishable from that of RSIL-2. A subsequent recovery of perchlorate from this solution, 151 days later, showed no significant change.

Chlorine Isotope Ratio Analyses

Chlorine isotope ratios (Table 2) were measured at the Environmental Isotope Geochemistry Laboratory of the University of Illinois at Chicago. Perchlorate salts were first decomposed at ~650°C in evacuated borosilicate glass tubes to produce alkali chloride salts, which were then analyzed according to well established methods.[30,31] The alkali chloride salts produced by perchlorate decomposition were dissolved in warm 18.2 MΩ deionized water, and Cl was precipitated as AgCl by addition of $AgNO_3$. The resulting AgCl was recovered by centrifugation, washed in dilute HNO_3, dried, and reacted in a sealed borosilicate glass tube with excess CH_3I at 300°C for two hours to produce CH_3Cl. The resulting CH_3Cl was purified cryogenically and/or using gas chromatography and then admitted to a Finnigan Delta-Plus XL isotope-ratio mass spectrometer and analyzed in dual-inlet mode by measurements at m/z 50 and 52, with the exception of the West Texas samples which were analyzed in continuous-flow mode. Samples were analyzed in replicate if sufficient amounts were available. Analytical yields of this procedure for reagent salts ranged from 81-97 % with no significant dependence of isotope ratio on yield. Chlorine isotope ratios are reported in units of $\delta^{37}Cl$, in terms of the per mil (‰) difference between the $^{37}Cl/^{35}Cl$ ratio of a sample and that of the isotopic reference material, Standard Mean Ocean Chloride (SMOC):[32,33]

$$\delta^{37}Cl\ (‰) = [(^{37}Cl/^{35}Cl)_{sample}/(^{37}Cl/^{35}Cl)_{SMOC} - 1] \times 1000$$

The analytical precision of $\delta^{37}Cl$ values reported in Table 2 ranges from ±0.1 to 0.3‰, based on replicate analyses of samples and isotopic reference materials.

Oxygen Isotope Ratio Analyses

Oxygen isotope ratios (Table 2) were measured at the Reston Stable Isotope Laboratory of the U.S. Geological Survey. Oxygen isotope ratios are reported as follows:[34]

$$\delta^{18}O\ (‰) = [(^{18}O/^{16}O)_{sample}/(^{18}O/^{16}O)_{VSMOW} - 1] \times 1000$$

$$\Delta^{17}O\ (‰) = [[(1 + \delta^{17}O/1000)/(1 + \delta^{18}O/1000)^{0.525}] - 1] \times 1000$$

For $\delta^{18}O$ determinations, perchlorate salts were reacted with glassy C at 1325°C to produce CO, which was transferred in a He carrier through a

Table 2.   Stable Isotope Ratios of Cl and O*

Sample Identification	$\delta^{37}Cl$	$\delta^{18}O$	$\Delta^{17}O$**
Laboratory Reagents			
UIC-1	+1.2	-16.2	+0.01
UIC-2	+1.1	-24.8	+0.01
UIC-3	+1.3	-16.1	+0.12
UIC-8	+0.5	-16.3	+0.02
UIC-9	+1.0	-17.2	0.00
UIC-10	+0.4	-12.5	-0.01
ORNL-6	-3.1	-17.2	+0.08
ORNL-8	+0.6	-19.1	+0.00
ORNL-9	+1.3	-16.4	+0.11
ORNL-10	+1.6	-16.6	-0.04
ORNL-11	+0.6	-16.9	+0.00
RSIL-2	n.a.	-14.6	+0.01
RSIL-4	+0.6	-17.0	+0.00
Production Materials			
UIC-5	+0.4	-22.3	-0.01
UIC-6	+0.4	-21.5	+0.07
UIC-7	+0.4	-21.3	-0.03
ORNL-18	+1.1	n.a.	+0.06
ORNL-19	+0.9	-20.4	+0.00
ORNL-20	n.a.	-13.5	n.a.
NaCl (TO415D)	+0.2	n.a.	n.a.
Natural Perchlorate			
ORNL-2	-13.7	-8.4	+8.95
ORNL-4	-14.5	-9.3	+8.93
ORNL-5	-11.8	-4.2	+9.57
ORNL-12	-14.2	-7.6	+9.25
Groundwater/ Surface Water			
ORNL-14	-0.9	-15.8	+0.04
ORNL-16	+0.4	-14.5	+0.00
ORNL-17	+0.9	-15.0	+0.02
ORNL-21	+6.2	+4.7	+0.42
ORNL-22	+5.1	+2.5	+0.49
CPMW-5	+0.2	n.a.	n.a.
TPMW-5	+1.1	n.a.	n.a.
Method Tests			
ORNL-15	-3.2	-17.2	n.a.
UIC-4	n.a.	-16.3	-0.13
RSIL-3	n.a.	-14.7	n.a.

*   All values reported in per mil

** $\Delta^{17}O = [[(1 + \delta^{17}O/1000) / (1 + \delta^{18}O/1000)^{0.525}] - 1] \times 1000$
    n.a. = not analyzed

molecular-sieve gas chromatograph to a Finnigan Delta Plus XP isotope-ratio mass spectrometer and analyzed in continuous-flow mode by monitoring peaks at m/z 28 and 30. Derived values of $\delta^{18}O$ were calibrated against VSMOW and SLAP by analyzing reference materials NBS-127 sulfate ($\delta^{18}O$ = +8.6 ‰), IAEA-N3 nitrate ($\delta^{18}O$ = +25.6 ‰), and USGS34 nitrate ($\delta^{18}O$ = -27.9 ‰) in a system equipped to prevent the N_2 peak from entering the ion source.[36] Yields of O (as CO) typically were within ± 2 per cent for ClO_4^-, NO_3^-, and SO_4^{2-} reagents and samples. The analytical precision of $\delta^{18}O$ values reported in Table 2 ranges from ±0.1 to 0.3 ‰, based on replicate analyses of samples and isotopic reference materials.
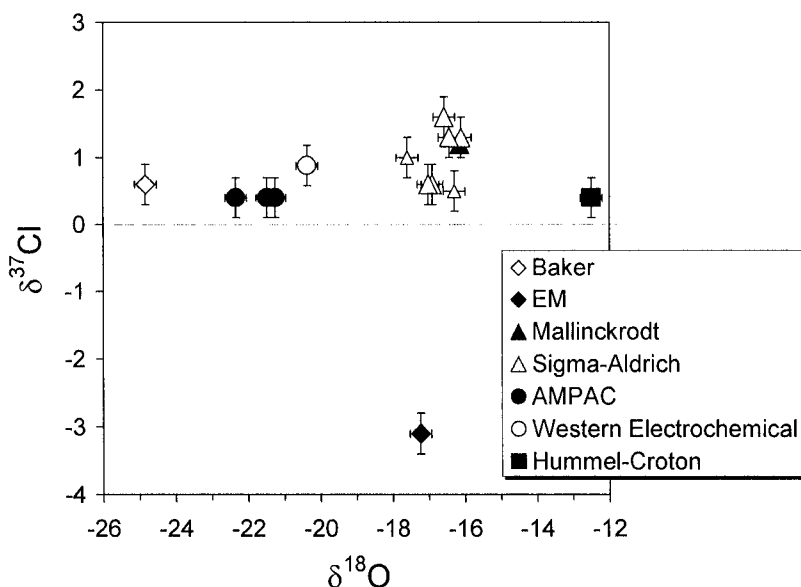
For $\Delta^{17}O$ determinations, perchlorate salts were decomposed for 12 minutes at 650°C in evacuated quartz glass tubes to produce O_2, then quenched in air. The O_2 gas was expanded into a liquid N_2 trap and then admitted to a Finnigan Delta Plus XP isotope-ratio mass spectrometer and analyzed in dual- inlet mode by measurements at m/z 32, 33, and 34. Yields of O (as O_2) typically were within ±5 percent for ClO_4^- reagents, ClO_4^- samples and measured aliquots of tank O_2. $\Delta^{17}O$ was assumed to be 0.00 ‰ for a representative $KClO_4$ reagent designated USGS37 (equal to the average of all anthropogenic ClO_4^- samples). This is consistent with derivation of the O from H_2O during ClO_4^- synthesis, and it results in a measured $\Delta^{17}O$ value of - 0.4 ‰ for tank O_2 from air. The apparent $\delta^{18}O$ difference between UIC-2 and RSIL-4 when analyzed as O_2 was about 0.92-0.96 times the normalized difference when analyzed as CO. Accordingly, the $\Delta^{17}O$ scale was expanded by a factor of 1.06 to account for O blank or exchange during ClO_4^- decomposition. The reproducibility of the $\Delta^{17}O$ measurements was ±0.1‰ or less after normalization, based on replicate analyses of samples and isotopic reference materials.

RESULTS AND DISCUSSION

Perchlorate Reagents and Production Materials

Samples of common reagent-grade perchlorate salts (Table 1) were obtained from the laboratory stocks of some of the authors. In addition, reactants used in the electrochemical synthesis of perchlorate (water and NaCl) as well as intermediate and final products ($NaClO_3$, $NaClO_4$, NH_4ClO_4, $NaClO_4$, and $KClO_4$) were obtained directly from the Western Electrochemical Company or from their parent company, AMPAC, the sole perchlorate supplier to the U.S. military since 1998. Chlorine and/or oxygen isotope ratios were measured in sixteen synthetic perchlorate salts, one chlorate salt, and one perchloric acid (Figure 2). The total range in measured $\delta^{37}Cl$ values of these

reagents is −3.1 to +1.6‰. Ader et al.[21] reported three $\delta^{37}Cl$ values for perchlorate reagents ranging from +0.2 to +2.3‰. Excluding sample ORNL-6, the range of $\delta^{37}Cl$ values in Table 2 is from +0.4 to +1.6 ‰. These values are near that of seawater chloride (0.0‰), reflecting the fact that the perchlorate in these materials is synthesized by electrochemical oxidation of brines derived from marine evaporite salt deposits (e.g., the sample of NaCl feedstock has a $\delta^{37}Cl$ value of +0.2‰), and that this process is relatively efficient with respect to Cl oxidation. This is demonstrated by data obtained for the series of samples obtained from the Western Electrochemical Company, including NaCl feedstock, $NaClO_3$ intermediate product, and $NaClO_4$ final product.

Figure 2. Isotopic composition of synthetic perchlorate salts, grouped by source according to symbols (see legend), displayed in a $\delta^{37}Cl$ vs. $\delta^{18}O$ diagram. Horizontal dashed line shows reference $\delta^{37}Cl$ value of SMOC (Standard Mean Ocean Chloride). Analytical error bars are shown at ±0.3 per mil. Isotopic differences between (and within) sources are significantly larger than the analytical precision.

The range in $\delta^{18}O$ values of synthetic perchlorate (−24.8 to −12.5‰) is significantly larger than that of $\delta^{37}Cl$ values, reflecting both a range in the local meteoric water compositions and the effect of mass-dependent isotopic fractionation involved in the perchlorate synthesis, which is relatively inefficient with respect to H_2O consumption. For example, there was a ~7‰ difference in $\delta^{18}O$ values of $NaClO_4$ (sample ORNL-19) and the local meteoric water used in its synthesis (sample ORNL-20) at the Western

Electrochemical Co. plant during June 2004. All samples of synthetic perchlorate have $\Delta^{17}O$ values of $0.0\pm0.1\permil$, indicating that neither the reactants nor the reaction mechanisms involved in perchlorate synthesis exhibit evidence for mass-independent isotopic fractionation.

Natural Perchlorate

Four samples of perchlorate were extracted from nitrate-bearing salts of the Atacama Desert and derivative fertilizer products, and their Cl and O isotopic compositions were measured (Table 2). The resulting $\delta^{37}Cl$ values range from -14.5 to $-11.8\permil$. These $\delta^{37}Cl$ values are much lower than the range of synthetic perchlorates reported in Table 2 (-3.1 to $+1.6\permil$). The $\delta^{18}O$ values of the natural perchlorate samples range from -9.3 to $-4.2\permil$, which is, in contrast, higher than that of synthetic perchlorates (-24.8 to $-12.5\permil$).

The most diagnostic isotopic characteristic of natural perchlorate is its positive $\Delta^{17}O$ value, which distinguishes natural perchlorate from synthetic perchlorate, which has $\Delta^{17}O = 0.0\pm0.1\permil$ on the scale adopted here. We measured $\Delta^{17}O$ values in the natural perchlorate ranging from $+8.93$ to $+9.57\permil$, confirming the earlier results obtained for similar materials.[23]

A graphical comparison of the isotopic compositions of all synthetic and natural perchlorate samples for which Cl and O isotope ratios were measured in this study is shown in Figures 3 and 4. The samples occupy two well-separated fields in the $\delta^{37}Cl$ vs $\delta^{18}O$ diagram (Figure 3). These data indicate that mixtures of synthetic and natural (Atacama) perchlorate should be identifiable, as should perchlorate that exhibits significant kinetic isotope effects caused by partial microbial or abiotic reduction. The $\Delta^{17}O$ vs $\delta^{18}O$ diagram (Figure 4) highlights the [17]O excess of natural perchlorate. The initially positive $\Delta^{17}O$ value found in the natural perchlorate should be unaffected by subsequent mass-dependent fractionation.

Groundwater and Surface Water

The distinct isotopic characteristics of synthetic and natural (Atacama) perchlorate may provide a simple tool with which to identify the source(s) of perchlorate in a given sample of groundwater or surface water, as well as the extent to which perchlorate is affected by subsurface chemical processes such as microbial or abiotic reduction. With these potential applications in mind, we extracted and analyzed perchlorate from groundwater at two military sites (Edwards Air Force Base, CA; and the Naval Surface Warfare Center, Indian Head Division, MD); groundwater and surface water from near the former Kerr-McGee perchlorate manufacturing site at Henderson,

NV; and groundwater from the West Texas panhandle area, where there is no known anthropogenic source of perchlorate. The groundwater and surface water samples from all of the military and industrial sites have a narrow range of $\delta^{37}Cl$ values (−0.9 to +1.1 ‰) that lies within the range of $\delta^{37}Cl$ values we found for synthetic perchlorate (−3.1 to +1.6 ‰) (Figure 3). Their measured $\delta^{18}O$ values (−15.8 to −14.5 ‰) are near the upper end of the range of $\delta^{18}O$ values we found for synthetic perchlorate (−24.8 to −14.6 ‰) (Figure 3), and their measured $\Delta^{17}O$ values were all identical to that of synthetic perchlorate (0.0±0.1‰) (Figure 4). These results indicate that the perchlorate in groundwater preserves the isotopic characteristics of its source, at least on a time scale of decades.
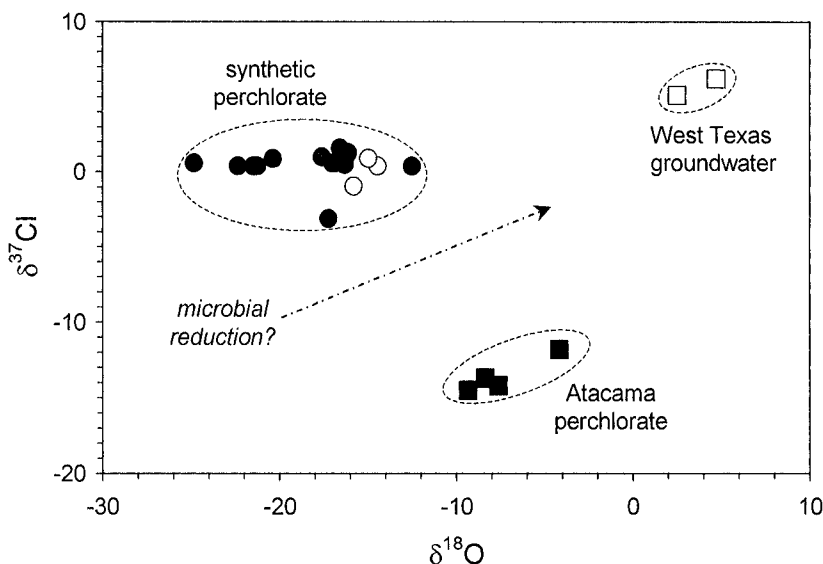

Figure 3.   Comparison of $\delta^{37}Cl$ and $\delta^{18}O$ values of synthetic (filled circles) and natural "Atacama-type" (filled squares) perchlorate. Also shown are groundwater and surface water perchlorate from military and industrial sites (open circles) and groundwater from West Texas (open squares) for which a synthetic source is unknown.[20] Dashed arrow indicates approximately the slope of the trajectory followed by residual perchlorate during partial microbial degradation according to preliminary experimental work.[22, 25, 26]

The results for the West Texas waters are interesting, because they fall outside the ranges that we found for $\delta^{37}Cl$, $\delta^{18}O$, and $\Delta^{17}O$ in all other perchlorate samples (Table 1, Figures 3 and 4). There are at least two plausible explanations for the anomalous isotopic ratios of the perchlorate in these West Texas groundwater samples:

i) The perchlorate is of natural origin, but it represents a type of natural perchlorate that is isotopically distinct from the Atacama perchlorate and has a formation mechanism that is currently unknown.

ii) The perchlorate is a mixture of synthetic perchlorate and "Atacama-type" natural perchlorate with an apparent mixing ratio based on $\Delta^{17}O$ of approximately 19:1 (synthetic:natural), This hypothesis assumes that oxygen exchange between perchlorate and water is negligible and requires that the mixture was significantly affected by mass-dependent isotopic fractionation associated with either microbial or abiotic reduction by about one-third.

Additional studies are underway to better define the origin of the West Texas perchlorate as well as that found at many other sites for which perchlorate sources are currently in question.
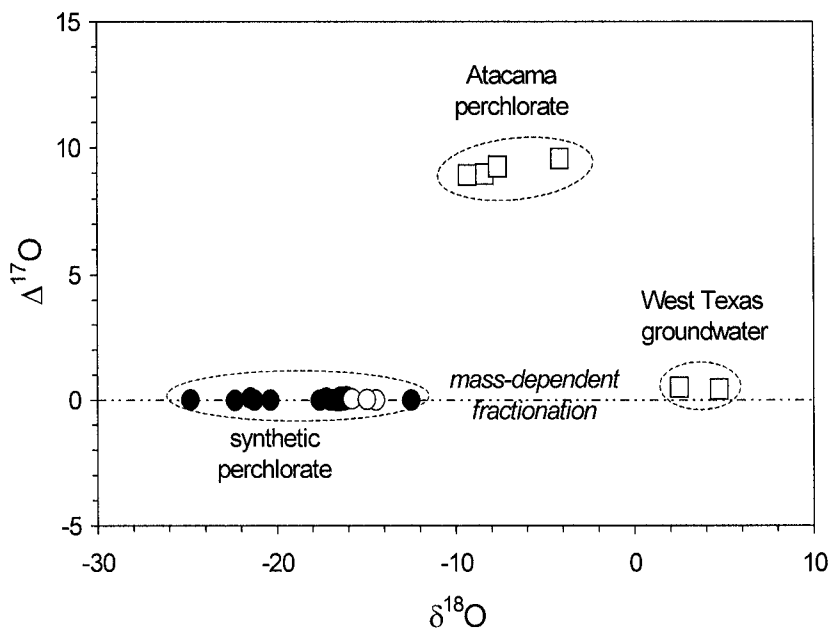

Figure 4.   Comparison of $\Delta^{17}O$ and $\delta^{18}O$ values of synthetic (filled circles) and natural "Atacama-type" (open squares) perchlorate. Also shown are groundwater and surface water perchlorate from military and industrial sites (open circles) and groundwater from West Texas (open squares) where there is no known synthetic source of perchlorate.[20] Dashed horizontal line at $\Delta^{17}O = 0$ indicates the slope of the trajectory followed by residual perchlorate during partial microbial degradation or other mass-dependent isotopic fractionation.[35]

SUMMARY AND CONCLUSION

Representative samples of perchlorate from a variety of synthetic and natural sources, along with trace amounts of perchlorate extracted from groundwater and surface water at several locations, have been analyzed for their Cl and O isotopic compositions. Large differences in Cl and O isotopic compositions were found between synthetic and natural sources of perchlorate. Synthetic perchlorate has $\delta^{37}Cl$ values from 0 to +2‰, $\delta^{18}O$ values from −25 to −12‰, and $\Delta^{17}O$ values of 0.0±0.1‰ (by definition in this study). Natural perchlorate is less well characterized as yet, but samples derived from nitrate-rich Atacama salts have $\delta^{37}Cl$ values from −15 to −11‰, $\delta^{18}O$ values from −10 to −4‰, and positive $\Delta^{17}O$ values around +9 to +10‰. These distinct isotopic characteristics may enable the use of stable isotopic analysis in forensic applications. In some cases, specific batches of synthetic perchlorate may be identified from their isotopic compositions. In addition, it should be possible to determine from measured isotopic composition whether dissolved perchlorate in groundwater is from a synthetic or natural source, or a mixture thereof.

A complicating factor in the application of isotopic measurements to tracing perchlorate in environmental samples is the potential for processes such as natural degradation or isotope exchange to alter the isotopic characteristics of dissolved perchlorate. Although the rates and isotope effects of such processes can be measured in the laboratory, few relevant laboratory studies have been done. Empirical evidence for the occurrence of perchlorate isotope effects in samples of groundwater and surface water also may be gained from additional field studies at well-characterized sites. Additional laboratory data on the kinetic isotope effects of various biotic and abiotic reduction mechanisms should be acquired to enable quantitative estimates of the extent of intrinsic degradation of perchlorate in contaminated aquifers.

Although the data compiled to date are intriguing, the reconnaissance study of perchlorate isotopic compositions reported herein is far from comprehensive. In order for isotope data of Cl and O in perchlorate to be useful and applicable from a forensic standpoint, a much broader database of these values must be obtained from both synthetic and natural sources. Moreover, the origin and behavior of perchlorate in a wide variety of natural settings must be explored in much greater detail.

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REFERENCES

1. Motzer W.E. Perchlorate: problems, detection, and solutions. Environ Forens 2001; 2: 301-311.

2. Urbansky E.T. Perchlorate as an environmental contaminant. Environ Sci Poll Res 2002; 3: 187-192.

3. Jackson P.E., Gokhale S., Streib T., Rohrer J.S., and Pohl C.A. Improved method for the determination of trace perchlorate in ground and drinking waters by ion chromatography. J Chrom A 2000; 888: 151-158.

4. Magnuson M.L., Urbansky E.T., Kelty C.A. Determination of perchlorate at trace levels in drinking water by ion-pair extraction with electrospray ionization mass spectrometry. Anal Chem 2000; 72: 25-29.

5. Jackson W. A., Joseph P., Patil L., Tan K., Smith P. N., Yu L., and Anderson T. A. Perchlorate accumulation in forage and edible vegetation. J Agricult Food Chem 2005; 53: 369-373.

6. Kirk A.B., Martinelango P. K., Tian K., Aniruddha D., Smith E. E., and Das Gupta P. K. Perchlorate and iodide in dairy and breast milk. Environ Sci Technol 2005; 39: 2011-2017.

7. Hogue C. Rocket-fueled river. Chem Eng News 2003; 81(33): 37-46.

8. Porterfield S.P. Vulnerabilities of the developing brain to thyroid abnormalities: environmental insults to the thyroid system. Environ Health Perspect 1994; 102: 125-130.

9. Wolff J. Perchlorate and the thyroid gland. Pharmacol Rev 1998; 50: 89-105.

10. National Research Council, *Health Implications of Perchlorate Ingestion.* Washington, D.C.: National Academies Press, 2005.

11. U. S. Environmental Protection Agency, National Center for Environmental Assessment, *Draft Perchlorate Risk Assessment.* Washington, D.C.: U. S. Govt Printing Press, 2002.

12. Hoering T. C., Ishimori F. T. and McDonald H. O. The oxygen exchange between oxyanions and water, 11. Chlorite, chlorate and perchlorate ions. J Amer Chem Soc 1958; 80: 3876.

13. Urbansky E.T. Perchlorate chemistry: implications for analysis and remediation. Bioremediation J 1998; 2: 81-95.

14. Coates J.D. and Achenbach L.A. Microbial perchlorate reduction: rocket-fuelled metabolism: Nature Rev Microbiol 2004; 2: 569-580.

15. Hatzinger P. B., Whittier M. C., Arkins M. D., Bryan C. W., and Guarini W. J. In-situ and ex-situ bioremediation options for treating perchlorate in groundwater. Remediation 2002; 12: 69-85.

16. Hatzinger, P. B. Perchlorate biodegradation for water treatment. Environ. Sci. Technol. 2005 (*In press*).

17. Ericksen, G.E. The Chilean nitrate deposits. Amer Scientist 1983; 71: 366-374.

18. Orris G. J., et al. Preliminary analyses for perchlorate in selected natural materials and their derivative products. U.S. Geol Surv Open-File Rept 03-314, 2003.

19. Dasgupta P. K., Martinelango P. K., Jackson W. A., Anderson T. A., Tian K., Tock R. W., and Rajagopalan S. The origin of naturally occurring perchlorate. Environ Sci Technol 2005; 39: 1569-1575.

20. Jackson W. A., Anandam S. K., Anderson T., Lehman T., Rainwater K., Rajagopalan S., Ridley M., and Tock R. Perchlorate occurrence in the Texas Southern High Plains Aquifer System. Ground Water Monitor Remed 2005; 25(1): 137-149.

21. Ader M., Coleman M.L., Doyle S.P., Stroud M., and Wakelin D. Methods for stable isotopic analysis of chlorine in chlorate and perchlorate compounds. Anal Chem 2001; 73: 4946-4950.

22. Sturchio N.C., Hatzinger P.B., Arkins M.D., Suh C., and Heraty L.J. Chlorine isotope fractionation during microbial reduction of perchlorate. Environ Sci Technol 2003; 37: 3859-3863.

23. Bao H. and Gu B. Natural perchlorate has a unique isotopic signature. Environ Sci Technol 2004; 38: 5073-5077.

24. Böhlke J.K., Sturchio N.C., Gu B., Horita J., Brown G.M., Jackson W.A., Batista J., and Hatzinger P.B. Perchlorate isotope forensics. Anal Chem 2005; 77: ##.

25. Coleman M.L., Ader M., Chaudhuri S., and Coates J.D. Microbial isotopic fractionation of perchlorate chlorine. Applied Environ Microbiol 2003; 69: 4997-5000.

26. Coleman M. L., Mielke R., and Coates J. D. Changes in Cl and O isotope compositions of perchlorate to measure extent of microbial reduction, but still identify the fingerprint of the original values. Geophys Res Abstr 2005; 7: 05954.

27. Böhlke J.K., Ericksen G.E., and Revesz K. Stable isotope evidence from an atmospheric origin of desert nitrate deposits in northern Chile and southern California, U.S.A. Chem Geol 2000; 136: 135-152.

28. Michalski G., Böhlke J.K., and Thiemens M.. Long term atmospheric deposition as the source of nitrate and other salts in the Atacama Desert, Chile: New evidence from mass-independent oxygen isotopic compositions. Geochim Cosmochim Acta 2004; 68: 4023-4038.

29. Gu B., Brown G. M., Maya L., Lance M. J., and Moyer B. A. Regeneration of perchlorate (ClO_4^-)-loaded anion-exchange resins by novel tetrachloroferrate ($FeCl_4^-$) displacement technique. Environ Sci Technol 2001; 35: 3363-3368.

30. Eggenkamp H.G.M. $\delta^{37}Cl$: The geochemistry of chlorine isotopes. Geologica Ultraiectina 1994; 116.

31. Holt B.D., Sturchio N.C., Abrajano T.A., and Heraty L.J. Conversion of chlorinated volatile organic compounds to carbon dioxide and methyl chloride for isotopic analysis of carbon and chlorine. Anal Chem 1997; 69: 2727-2733.

32. Long A., Eastoe C.J., Kaufmann R.S., Martin J.G., Wirt L., and Finley J.B. High-precision measurement of chlorine stable isotope ratios: Geochim Cosmochim Acta 1993; 57: 2907-2912.

33. Godon A., Jendrzejewski N., Eggenkamp H.G.M., Banks D.A., Ader M., Coleman M.L., and Pineau F. An international cross calibration over a large range of chlorine isotope compositions. Chem Geol 2004; 207: 1-12.

34. Miller M. F. Isotopic fractionation and the quantification of ^{17}O anomalies in the oxygen three-isotope system: an appraisal and geochemical significance. Geochim Cosmochim Acta 2002; 66: 1881-1889.

35. Böhlke J.K., Mroczkowski S.J., Coplen T.B. Oxygen isotopes in nitrate: new reference materials for ^{18}O:^{17}O:^{16}O measurements and observations on nitrate-water equilibration. Rapid Commun Mass Spec 2003; 17: 1835-1846.